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Allan N. Kaufman and Kenneth M. Watson
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ABSTRACT

By means of the linked-diagram expansion of the grand partition function of a molecular gas in an electrostatic field, an expression for the polarization $P(R)$ of the gas is obtained. Spatial variation of the external electric field $E_0(R)$ requires an explicit treatment of long-range cooperative interactions between "clusters" of molecules. For fields that vary appreciably over microscopic dimensions, an integral relation is found relating the polarization $P(R)$ to the electric field $E(R)$. For fields varying negligibly over microscopic regions, an expression for the dielectric constant $K$ of the gas is obtained:

$$
\frac{K - 1}{K + 2} = \frac{4\pi}{3} \sum_{m=1}^{\infty} \frac{z^m}{m} \alpha'_m(\Theta).
$$

This generalization of the Clausius-Mossotti formula involves the activity $z$ and the temperature-dependent polarizability $\alpha'_m$ of an $m$-molecule linked cluster.
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I. INTRODUCTION

Statistical mechanics provides a method of calculating the properties of a system in thermodynamic equilibrium from an evaluation of the partition function. Recently diagrammatic techniques have been developed to enable one to perform this evaluation for a many-body system. In a previous paper, which will be referred to as I, we applied the technique developed by Glassgold, Heckrotte, and Watson to the system of a gas of neutral molecules, taking into account the structure of the molecules and the operation of the Pauli principle among all the electrons of the system; the nuclei in different molecules were, however, treated as distinguishable, and the motion of the molecular centers of mass was treated classically. The result of that paper was the well-known Ursell-Mayer expansion, with the classical cluster integrals suitably generalized for molecular structure and the Pauli principle. This generalization had previously been obtained by a different method by Ono and Kilpatrick.

The present paper applies the method of I to the system of a gas of neutral molecules in an external electrostatic field. In contrast to I, the interaction of the molecules now has a long-range (dipole-dipole) contribution. Response of the system to the field is characterized by the polarization, or mean dipole density, of the gas. In Sec. II, after some preliminaries, we

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relate the dipole density to the Hamiltonian (Eq. 2.19). In Sec. III the polarization is then related to the grand partition function (Eq. 3.2), and contact is made with classical electrostatic theory. In this paper we consider only the linear term in the relation between the external field and the polarization; the required formulas are quoted from I at the end of Sec. III. Evaluation proper begins with a discussion of single-molecule graphs (see Fig. 1) in Sec. IV, leading to the concept of polarizability. It is shown that polar and nonpolar molecules can be treated in the same way. Section V then takes up a particularly simple type of graph (called a simple chain; see Fig. 2), in which each molecule has just two interactions. The Hugenholtz theorem (Appendix A) is used to evaluate the sum of all simple chains; we believe that the technique employed should be useful also in other calculations.

Section VI is devoted to an evaluation of the "cluster chains" (see Fig. 6); this type of graph separates short- and long-range interactions. The result of the calculation is a series for the Clausius-Mossotti function in powers of the activity (Eqs. 6.27 and 6.28). The coefficients of the series are functions of the temperature and are the polarizabilities (Eq. 6.29) of m-molecule linked clusters. Equation (6.34) is the corresponding expansion in powers of the density, and involves also the zero-field cluster integrals. Finally, it is shown that only cluster chains contribute appreciably to the partition function, so that the approximation of keeping only such graphs is a satisfactory one.

In a subsequent paper we shall discuss the explicit evaluation of the m-molecule polarizabilities, and shall relate our results to those of previous investigators.
II. MOLECULAR DYNAMICS

We consider a gas of \( N \) neutral molecules, of a single species, contained in a volume \( V \). The only external field acting on the gas is an electrostatic field \( \mathbf{E}_0(\mathbf{r}) \), due to fixed charge sources. When the gas is removed, \( \mathbf{E}_0(\mathbf{r}) \) is the actual field; but in the presence of the gas, the total field \( \mathbf{E}(\mathbf{r}) \) includes also the field due to the polarization of the molecules of the gas. We propose to evaluate the field \( \mathbf{E} \) and the polarization, using the "linked diagram" expansion of I.

As in I, we use Boltzmann statistics for the molecules, and number them \( i = 1, \ldots, N \). Let \( \mathbf{R}_i \) be the position operator of the center of mass of the \( i \)th molecule, and let \( \mathbf{x}_\rho \) be the position operator of the \( \rho \)th particle (electron or nucleus) relative to the center of mass of the molecule. The charge density operator of the \( i \)th molecule is thus

\[
\varepsilon_i(\mathbf{r}) = \sum_\rho q_\rho \delta(\mathbf{r} - \mathbf{x}_\rho),
\]

where \( q_\rho \) is the charge of the \( \rho \)th particle. Because of the assumed neutrality of the molecules, we have

\[
\int d^3 r \, \varepsilon_i(\mathbf{r}) = 0.
\]

The Coulomb interaction energy of two molecules is

\[
V_{ij} = \int d^3 r \, \int d^3 r' \, \varepsilon_i(\mathbf{r}) \, \varepsilon_j(\mathbf{r'}) \left| (\mathbf{R}_i + \mathbf{r}) - (\mathbf{R}_j + \mathbf{r'}) \right|^{-1},
\]

and the total Coulomb interaction energy is

\[
V_{\text{int}} = \sum_{i<j} V_{ij}.
\]
When the separation $R_{ij} = R_i - R_j$ of two molecules is large compared with molecular dimensions, the interaction energy (Eq. 2.3) reduces to

$$V_{ij} = \mathcal{P}_i \cdot \mathcal{A}_{ij} \cdot \mathcal{P}_j,$$

(2.5)

where

$$\mathcal{P}_i = \int d^3r \, \mathbf{\epsilon}_i(x) = \sum_p \mathbf{q}_p \mathbf{L}_p$$

(2.6)

is the electric dipole moment (operator) of the $i$th molecule, and

$$\mathcal{A}_{ij} = \mathcal{A}(R_i, R_j) = \nabla_i \cdot \nabla_j R_{ij}^{-1} = (\mathbf{L} R_{ij}^2 - 3 \mathbf{R}_{ij} \mathbf{R}_{ij}) R_{ij}^{-5},$$

(2.7)

with $\mathbf{L}$ the unit dyadic.

The energy of interaction of the $i$th molecule with the external field $E_0$ is

$$V_i = \int d^3r \, \mathbf{\epsilon}_i(x) \cdot \mathbf{\varphi}_0(R_i + x),$$

(2.8)

where $\mathbf{\varphi}_0$ is the external potential: $E_0 = -\nabla \mathbf{\varphi}_0$; the total external interaction energy is

$$V_{ext} = \sum_i V_i.$$

(2.9)

We shall suppose that the external field is macroscopic, in that $E_0$ is effectively constant over any region whose dimensions are of the order of the size of a molecule. Then, with Eq. (2.2), (2.8) reduces to

$$V_i = -\mathcal{P}_i \cdot E_0(R_i).$$

(2.10)

Let $h_i$ be the Hamiltonian of the isolated $i$th molecule. As discussed in I, $h_i$ is an operator with respect to those electrons assigned
to molecule $i$. It includes interactions among these electrons and with the nuclei of $i$, but excludes their interactions with electrons and nuclei in other molecules. The (properly antisymmetrized) eigenstates and eigenvalues of $h_i$ are given by

$$
h_i \left| \lambda_1 \right> = \left[ (k_1^2/2M) + e_i \right] \left| \lambda_1 \right> .
$$

(2.11)

Because $h_i$ is invariant under the parity operation, we may in case of degeneracy choose the states $\left| \lambda_1 \right>$ to be parity eigenstates. It follows that the dipole operator has no diagonal elements:

$$
\left< \lambda_1 \left| p_{x1} \left| \lambda_1 \right> = 0 .
\right.
$$

(2.12)

The total Hamiltonian is

$$
H = K + v^{\text{int}} + v^{\text{ext}} ,
$$

(2.13)

where

$$
K = \Sigma_i h_i
$$

(2.14)

is the Hamiltonian for noninteracting molecules. The eigenstates of $K$ are products of those of $h_i$:

$$
K \left| \Lambda \right> = E_{\Lambda} \left| \Lambda \right> ,
$$

(2.15)

where

$$
\left| \Lambda \right> = \prod_i \left| \lambda_i \right> .
$$

(2.16)

Although $H$ is invariant under electron interchange between molecules, $K$ is not, since it selects interactions according to the assignment of the electrons to the molecules. Thus the states $\left| \Lambda \right>$ do not satisfy the
Pauli principle. In I we have shown how to take the Pauli principle into account when doing a perturbation calculation in $v_{\text{int}} + v_{\text{ext}}$.

Let us introduce the dipole density operator,

$$ P(R) = \Sigma_i \epsilon_i \delta(R - R_i). \quad (2.17) $$

The external interaction can now be written as

$$ v_{\text{ext}} = - \int d^3R P(R) \cdot E_0(R). \quad (2.18) $$

Thus the dipole density can be expressed as a functional derivative of the Hamiltonian:

$$ P(R) = - \frac{\delta H}{\delta E_0(R)} . \quad (2.19) $$
III. STATISTICAL MECHANICS

The properties of the gas in thermal equilibrium are derivable from the grand partition function

$$\mathcal{Z}(\theta, \mu, V, E_0(R)) = \sum_N (N!)^{-1} e^{\mu N} \text{Tr} e^{-\beta H}, \quad (3.1)$$

where $\theta = \beta^{-1}$ is the temperature of the gas, $\mu$ is its chemical potential, and $V$ represents the volume of the particular vessel containing the gas. We define the polarization as the statistical mean of the dipole density,

$$\langle \mathcal{R} \rangle(R) = \mathcal{Z}^{-1} \sum_N (N!)^{-1} e^{\mu N} \text{Tr} \left[ e^{-\beta H} \left[ -\delta H / \delta E_0(R) \right] \right]$$

$$= \theta \delta \ln \mathcal{Z} / \delta E_0(R). \quad (3.2)$$

In terms of the thermodynamic potential $\Omega = -\theta \ln \mathcal{Z}$, this reads

$$\delta \Omega = -\int d^3 R \langle \mathcal{R} \rangle(R) \cdot \delta E_0(R), \quad (3.3)$$

where $\theta$, $\mu$, and $V$ are held constant. In our subsequent discussion, we shall drop the angular bracket notation on $\langle \mathcal{R} \rangle$ and let it be understood.

We follow Brown in defining the macroscopic field $E(R)$ as the sum of the external field and that due to the macroscopic polarization:

$$E(R) = E_0(R) - \nabla \int d^3 R' \frac{E(R') \cdot \nabla R}{|R - R'|^{1}}, \quad (3.4)$$

As we have shown elsewhere, this field differs in general from the statistical mean of the microscopic field; but it is the appropriate definition for the development of macroscopic electrostatics. Since the integrand of the second term is singular at $R = R'$, let us exclude an infinitesimal sphere about $R$ from the integration volume; this does not change the value of the integral. We may then perform the operation $\nabla R$...
on both the integrand and the limits of integration, and find

$$E(R) = E_0(R) - \int d^3R' A(R, R') \cdot \mathbf{P}(R') - \frac{4\pi}{3} \mathbf{P}(R). \quad (3.5)$$

The prime on the integral sign indicates that an infinitesimal sphere is to be excluded. We now use the fact that $\mathbf{P}(R)$ varies only macroscopically to replace the infinitesimal sphere by one of finite but macroscopically small radius $R_0$. This is possible because the angular integration of $A$ vanishes.

We see from Eq. (3.4) that $E$ satisfies

$$\nabla \times E = 0 \quad (3.6)$$

and

$$\nabla \cdot E = \nabla \cdot E_0 - 4\pi \nabla \cdot \mathbf{P}. \quad (3.7)$$

As usual we introduce the conventional definition of the displacement field

$$D = E + 4\pi \mathbf{P}, \quad (3.8)$$

whose sources are those of the external field

$$\nabla \cdot D = \nabla \cdot E_0. \quad (3.9)$$

The energy of the external sources is

$$U_0 = \int d^3R \ E_0^2 / 8\pi, \quad (3.10)$$

and satisfies

$$8 U_0 = (4\pi)^{-1} \int d^3R \ E_0 \cdot \delta E_0. \quad (3.11)$$

Let us now use the theorem that for two fields $\mathbf{A}, \mathbf{B}$ satisfying

$$\nabla \cdot \mathbf{A} = 0, \ \nabla \times \mathbf{B} = 0,$$

the spatial integral of their scalar product vanishes:

$$\int d^3R \ A(R) \cdot B(R) = 0. \quad (3.12)$$
We can then write Eq. (3.11), with the help of (3.9), as

\[ \delta U_0 = \left( \frac{4\pi}{k} \right)^{-1} \int d^3R \cdot \mathbf{E} \cdot \delta \mathbf{E}_0 , \]  

(3.13)

and add it to Eq. (3.3):

\[ \delta(\Omega + U_0) = \left( \frac{4\pi}{k} \right)^{-1} \int d^3R \mathbf{E} \cdot \delta \mathbf{E}_0 . \]

(3.14)

Using Eqs. (3.12), (3.9), and (3.6), we then obtain the well-known relation for the total free energy,

\[ \delta(\Omega + U_0) = \left( \frac{4\pi}{k} \right)^{-1} \int d^3R \mathbf{E} \cdot \delta \mathbf{E}_0 , \]

(3.15)

where \( \theta, \mu, \) and \( \mathcal{V} \) are held constant.

It is evident that \( \Omega \) must be an even functional of \( \mathbf{E}_0(R) \). In this paper we confine our attention to the lowest nonvanishing effects of \( \mathbf{E}_0 \), those of second order. The polarization is then a linear functional of \( \mathbf{E}_0 \), and Eq. (3.3) can be integrated to

\[ \Omega(\theta, \mu, \mathcal{V}, \mathbf{E}_0) = \Omega(\theta, \mu, \mathcal{V}, 0) - \frac{1}{2} \int d^3R \mathbf{E}(R) \cdot \mathbf{E}_0(R) , \]

(3.16)

which we abbreviate as

\[ \Omega = \Omega^{(0)} + \Omega^{(2)} , \]

(3.17)

with

\[ \Omega^{(2)} = -\frac{1}{2} \int d^3R \mathbf{E}(R) \cdot \mathbf{E}_0(R) . \]

(3.18)

The linked-diagram expansion of I enables us to evaluate Eq. (3.18) and thus to find the linear relationship of \( \mathbf{E} \) to \( \mathbf{E}_0 \). As one expects, this is of the form

\[ \mathbf{E}(R) = \mathcal{X} \mathbf{E}_0(R) , \]

(3.19)
if $E_0$ varies inappreciably over the distance $R_0$. Because of our restriction to linearity in Eq. (3.19), $X$ is necessarily of zero order in $E_0$ and is thus independent of position, depending only on temperature and chemical potential. In a subsequent publication we plan to investigate nonlinear effects, which will determine the spatial variation of $X$ and of density, as well as explicit modification of the form of (3.19).

In Eq. (3.35) of I, we showed that $\ln \frac{\bar{Z}}{\bar{C}}$ could be expressed as

$$\ln \frac{\bar{Z}}{\bar{C}} = \sum_{m=1}^{\infty} \frac{F_m}{m!}, \quad (3.20)$$

where

$$F_m = (m!)^{-1} \frac{e^{\mu m}}{m} \lim_{\beta \to 0} \left[ \text{Tr} \exp(-\beta H^m) \right] \quad (3.21)$$

represents the contribution of all $m$-molecule linked graphs. The total Hamiltonian for the $m$ molecules is $H^m$, the trace is over properly antisymmetrized states for all the electrons of the $m$ molecules, and the operator $L_m$ selects the linked graphs, as explained in I.

As in Sec. IV of I, we shall treat the molecular center-of-mass motion classically, obtaining

$$F_m = (m!)^{-1} \left( \frac{e^{\mu m}}{m!} \right)^m \int d^3R^m \left[ \text{Tr} \exp(-\beta H^m(R^m)) \right]. \quad (3.22)$$

Here $\lambda$ is the thermal wave length

$$\lambda = \left( \frac{2\pi M\theta}{k_b} \right)^{1/2}, \quad (3.23)$$

and $H^m(R^m)$ differs from $H^m$ by omitting the center-of-mass kinetic energy terms $k_b \frac{k^2}{2M}$. Henceforth this omission will be implicitly understood.
also in $K$ and $h_{1}$ of Eqs. (2.11) and (2.14). Again we introduce the activity

$$z = \gamma e^{\beta \mu} / \lambda^{3},$$

(3.24)

where

$$\gamma = \sum_{\lambda} e^{-\beta e(\lambda)}$$

(3.25)

is the single-molecule internal partition function in the absence of a field, and $e(\lambda)$ is the molecular energy defined by Eq. (2.11). We then have, in the linear approximation,

$$\mathcal{P}(\mathcal{R}) = \theta \sum_{m=1}^{\infty} 8 \mathcal{F}_{m}^{(2)} / 8 \mathcal{E}_{0}(\mathcal{R}),$$

(3.26)

where

$$\mathcal{F}_{m}^{(2)} = (z^{m} / \gamma^{m} m!) \mathcal{L}_{m}^{(2)} \left\{ \int d^{3}R^{(m)} \text{Tr} \exp[-\beta H_{m}^{R}(R^{(m)})] \right\}$$

(3.27)

and $\mathcal{L}_{m}^{(2)}$ selects $m$-molecule linked graphs with two external interactions.
Fig. 1.
IV. THE SINGLE-MOLECULE POLARIZABILITY

As an introduction to our study of m-molecule graphs, we consider here the simple case \( m = 1 \), i.e., the single-molecule graph, shown in Fig. 1. The contribution to the polarization (Eq. 3.26) is

\[
P_m(R) = \delta \delta F_1^{(2)}/\delta E_0(R) ,
\]

with

\[
F_1^{(2)} = (z/\gamma) L^{(2)} \left\{ \int d^3R_1 \text{Tr} \exp[-\beta H_1^{(R_1)}] \right\} .
\]

The one-molecule Hamiltonian is

\[
H_1^{(R_1)} = h_1 + V_1(R_1) ,
\]

with

\[
V_1(R_1) = -p_{R_1} \cdot E_0(R_1) .
\]

Following I, we introduce the Laplace transform,

\[
F_1^{(2)} = (z/\gamma) \int d^3R_1 L^{(2)} \left\{ \text{Tr} (2\pi i)^{-1} \int dw e^{-\beta w} [w - H_1^{(R_1)}]^{-1} \right\} ,
\]

and expand the factor \([w - H_1^{-1}]\) in \(V_1\), keeping only the term with two factors of \(V_1\):

\[
F_1^{(2)} = (z/\gamma) \int d^3R_1 \text{Tr} (2\pi i)^{-1} \int dw e^{-\beta w} (w - h_1)^{-1} V_1(w - h_1)^{-1} V_1(w - h_1)^{-1} .
\]

We note the identity

\[
\text{Tr}(w - h_1)^{-1} V_1(w - h_1)^{-1} V_1(w - h_1)^{-1} = -\frac{1}{2} \text{Tr} \frac{d}{dw} \left\{ (w - h_1)^{-1} V_1(w - h_1)^{-1} V_1 \right\} ,
\]

(4.7)
substitute into Eq. (4.6), and integrate by parts to obtain

\[ F_1(2) = -\frac{1}{2} \beta(z/3) \int d^3R_1 \text{Tr}(2\pi i)^{-1} \int dw e^{-\beta w} (w - h_1)^{-1} V_1(w - h_1)^{-1} V_1. \]  

(4.8)

This expression differs from Eq. (4.6) by the extra factor \((-\frac{1}{2} \beta)\) and one less factor \((w - h_1)^{-1}\).

We substitute the explicit form of \(V_1\) (Eq. 4.4) and write this as

\[ F_1(2) = \frac{1}{2} \beta z \int d^3R_1 E_0(R_1) \cdot \mathcal{A}_1 \cdot E_0(R_1), \]  

(4.9)

where

\[ \mathcal{A}_1 = \gamma^{-1} \text{Tr}(2\pi i)^{-1} \int dw e^{-\beta w} (w - h_1)^{-1} p_1(w - h_1)^{-1} p_1 \]  

(4.10)

is the molecular polarizability. From Eq. (4.1) the polarization is, to this order,

\[ \mathcal{E}_1(R) = z \mathcal{A}_1 \cdot E_0(R). \]  

(4.11)

In the low-density limit that the contribution of \(m > 1\) may be neglected, the activity \(z\) reduces to the density \(n\), and we have the elementary result

\[ \mathcal{E}(R) = n \mathcal{A}_1 \cdot E_0(R). \]  

(4.12)

Let us express \(\mathcal{A}_1\) in terms of molecular matrix elements and eigenvalues.

Introducing the eigenstates of \(h_1\) in Eq. (4.10), we have

\[ \mathcal{A}_1 = -\gamma^{-1} \sum_{\lambda\lambda'} (2\pi i)^{-1} \int dw e^{-\beta w} (w - e')^{-1} (w - e)^{-1} \chi(\lambda \mid p_1 \mid \lambda') \chi(\lambda' \mid p_1 \mid \lambda). \]  

(4.13)
We assume, for simplicity, that the states are nondegenerate; because of Eq. (2.12), there are then only simple poles, yielding

\[
\alpha_1 = -\gamma^{-1} \sum_{\lambda \lambda'} (e' - e)^{-1} [\exp(-\beta e') - \exp(-\beta e)] \langle \lambda | p_1 | \lambda' \rangle \langle \lambda' | p_1 | \lambda \rangle
\]

(4.14a)

\[
= 2\gamma^{-1} \sum_{\lambda} e^{-\beta e} \sum_{\lambda'} (e' - e)^{-1} \langle \lambda | p_1 \rangle \langle \lambda' | p_1 | \lambda \rangle \rangle 
\]

(4.14b)

Because of the isotropy of \( h \) and the hermiticity of \( p_1 \), this becomes

\[
\alpha_1 = \alpha_1(\theta) \mathbb{1},
\]

(4.15)

with

\[
\alpha_1(\theta) = 2\gamma^{-1} \sum_{\lambda} e^{-\beta e} \sum_{\lambda'} (e' - e)^{-1} |\langle \lambda | p_{1z} | \lambda' \rangle|^2
\]

(4.16)

and

\[
\alpha_1(\lambda) = 2 \sum_{\lambda'} (e' - e)^{-1} |\langle \lambda | p_{1z} | \lambda' \rangle|^2.
\]

(4.17)

Equation (4.17) is the well-known formula for the polarizability of a system in a given state, and (4.16) is its statistical mean.

The classical polarizability of a polar molecule may be obtained from Eq. (4.14a) by assuming that \( \langle \lambda | p_1 | \lambda' \rangle \) is nonvanishing only for states differing in energy by an amount much less than the temperature. We can then write

\[
(e' - e)^{-1} [\exp(-\beta e') - \exp(-\beta e)] = \frac{d}{de} e^{-\beta e}
\]

\[= -\beta e^{-\beta e},
\]
so that Eq. (4.14a) becomes

$$\alpha_1 = \tau^{-1} \beta \sum_{\lambda \lambda'} e^{-\beta e} \langle \lambda | p_{\lambda} | \lambda' \rangle \langle \lambda' | p_{\lambda'} | \lambda \rangle$$

$$= \tau^{-1} \beta \sum_{\lambda} e^{-\beta e} \langle \lambda | p_{\lambda} p_{\lambda} | \lambda \rangle$$

$$= \beta \langle p_{\lambda} p_{\lambda} \rangle,$$

or

$$\alpha_1(\theta) = \frac{1}{3} \text{Sp} \alpha_1 = \frac{1}{3} \beta \langle p_{\lambda}^2 \rangle,$$  \hspace{2cm} (4.18)

the well-known classical formula. For further discussion of $\alpha_1$, one can refer to the treatise of Van Vleck.\textsuperscript{15}
V. SIMPLE CHAINS

In this section we consider the contribution of a special class of graphs, to be denoted as "simple chains." We define a simple chain as an m-molecule linked graph (with two external interactions) in which each molecule has two and only two interactions, and for which electron exchange is neglected. Figure 2 illustrates a simple chain for \( m = 3 \). Let \( F_m^{sc} \) denote the contributions of simple chains to \( F_m^{(2)} \). (Note that \( F_1^{sc} = F_1^{(2)} \).) Then \( F_m^{sc} \) is given by Eq. (3.27), with \( L_m^{(2)} \) replaced by \( L_m^{sc} \), which selects all simple chains.

The \( m \) molecules of the chain may be ordered in \( \frac{1}{2} (m!) \) different ways, for \( m > 1 \). (The factor \( \frac{1}{2} \) arises from the fact that a given chain order from left to right is not different from the same order from right to left.) Hence we may set \( L_m^{sc} = \frac{1}{2} (m!) L_m^{osc} \), where the latter operator selects chains whose molecules are ordered \( 1, \ldots, m \) from left to right. Thus Eq. (3.27) becomes

\[
F_m^{sc} = \frac{1}{2} \left( \frac{z}{\gamma} \right)^m L_m^{osc} \left\{ \int dR^{(m)} \operatorname{Tr} \exp[-\beta H^{m}(R^{(m)})] \right\} . \tag{5.1}
\]

We follow the method of I in developing the perturbation expansion for Eq. (5.1):

\[
\exp[-\beta H^{m}(R^{(m)})] = (2\pi i)^{-1} \int dW e^{-\beta W} [W - H^{m}(R^{(m)})]^{-1} , \tag{5.2}
\]

\[
L_m^{osc} \left\{ [W - H^{m}(R^{(m)})]^{-1} \right\} = \Sigma_p (W - K^m)^{-1} V_\mu (W - K^m)^{-1} V_\nu \cdots V_\sigma (W - K^m)^{-1} . \tag{5.3}
\]

In this expression \( K^m \) is the sum of the internal Hamiltonians of the \( m \) molecules, and the \( V \)'s represent the set of \( (m + 1) \) different interactions of the molecules in the simple chain: \( V_1, V_{12}, V_{23}, \ldots, V_{m-1m}, V_m \). The
Fig. 2.
sum is over the \((m + 1)!\) different "chronological orders" of these interactions. We speak of the lowest interaction on the graph as being the "earliest," and place it on the right in Eq. (5.3). For example, the term of Eq. (5.3) representing Fig. 2 has the \(V's\) in the order \(V_1, V_{23}, V_3, V_{12}\) from left to right in Eq. (5.3), or from top to bottom or "latest" to "earliest" in Fig. 2.

For a given term (or graph) of Eq. (5.3), we perform a partial sum over graphs differing from it only by a cyclic permutation of the \(V's\). Such a graph is shown in Fig. 3. With \(\Sigma_c\) representing the sum over cyclic permutations, we have

\[
\text{Tr} \Sigma_c (W - K^m)^{-1} V_{\mu} (W - K^m)^{-1} V_{\nu} \cdots V_{\sigma} (W - K^m)^{-1}
= - \frac{d}{dW} \text{Tr} V_{\mu} (W - K^m)^{-1} V_{\nu} \cdots V_{\sigma} (W - K^m)^{-1},
\]

(5.4)

analogous to Eq. (4.7). We then insert Eqs. (5.2) and (5.3) into (5.2), use (5.4), and integrate by parts:

\[
F_m^{sc} = - \frac{1}{2} \beta (z / \gamma)^m \int d^2 R (m) \text{Tr} (2\pi i)^{-1} \int dW e^{-\beta W} \Sigma P V_{\mu} \cdots V_{\sigma} (W - K^m)^{-1},
\]

(5.5)

where the primed summation is over noncyclic permutations of the \(V's\).

Because of the trace operation, each term of the summand may be cyclically permuted so that \(V_{12}\) stands on the left, as in Fig. 3. The expression then becomes

\[
F_m^{sc} = - \frac{1}{2} \beta (z / \gamma)^m \int d^2 R (m) \text{Tr} V_{12} (2\pi i)^{-1} \int dW e^{-\beta W} \Sigma P (W - K^m)^{-1} V_{\mu} \cdots V_{\sigma} (W - K^m)^{-1},
\]

(5.6)

with the sum over all permutations of the \(V's\) exclusive of \(V_{12}\).
Fig. 3.
The summand now represents an unlinked graph, between different initial and final states (see Fig. 4), and so is subject to the Hugenholtz theorem (Appendix). By Eq. (A.1), we have

\[(2\pi i)^{-1} \int dW e^{-\beta W} \Sigma_{p}(W - K^{-1})^{-1} V_{\mu} \cdots V_{\sigma}(W - K^{-1})^{-1} \]

\[= (2\pi i)^{-1} \int dW e^{-\beta W(W - K^{-1})^{-1}} V_{\mu} \cdots V_{\sigma}(W - K^{-1})^{-1} \]

\[\times (2\pi i)^{-1} \int dw e^{-\beta w(w - h_{1})^{-1}} V(w - h_{1})^{-1} . \]

The first factor on the right side has a particular order of V's exclusive of V_{12} and V_{11}, while the left side has the same order of these V's, but sums over all positions of V_{1} among them. In Eq. (5.6) one must still sum over all permutations of these V's:

\[P_{m}^{sc} = -\frac{1}{2} \beta(z/r)^{m} \int d^{2}R^{(m)} \text{Tr} V_{12}(2\pi i)^{-1} \int dW e^{-\beta W} \]

\[\times \Sigma_{p}(W - K^{-1})^{-1} V_{\mu} \cdots V_{\sigma}(W - K^{-1})^{-1} \]

\[\times (2\pi i)^{-1} \int dw e^{-\beta w(w - h_{1})^{-1}} V(w - h_{1})^{-1} . \]

The contribution of \(P_{m}^{sc}\) to the polarization is (see Eq. 3.26).

\[P_{m}^{sc}(R) = 85 P_{m}^{sc} / E_{0}(R) . \]

Now \(E_{0}\) appears in \(P_{m}^{sc}\) only through \(V_{m}(R_{m})\) and \(V_{1}(R_{1})\) (see Eq. 2.10). Since \(V_{1}\) appears explicitly in expression (5.8), we may perform the differentiation of (5.9) with respect to \(V_{1}\) only, and multiply by 2 to take account of \(V_{m}\):
Fig. 4
where […] represents the expression in brackets of Eq. (5.8).

If we introduce \(|\lambda_1\rangle\) and \(|\Lambda^{(m-1)}\rangle\), the eigenstates of \(h_1\) and \(K^{m-1}\) respectively, we may write this as

\[
P_{m}^{sc}(R) = \frac{z}{\gamma} \sum_{\lambda_1, \lambda'_1} p_\lambda(\lambda'_1, \lambda_1) Q_m(R; \lambda_1, \lambda'_1),
\]  

(5.11)

with

\[
p_\lambda(\lambda'_1, \lambda_1) = (2\pi i)^{-1} \int dw e^{-\beta W}(w - e'_1)^{-1} (\lambda'_1 | \lambda_1)(w - e_1)^{-1} \left(\exp(-\beta e'_1) - \exp(-\beta e_1)\right),
\]  

(5.12)

and

\[
Q_m(R; \lambda_1, \lambda'_1) = \left(\frac{z}{\gamma}\right)^{m-1} \int d^3 R^{(m-1)} \sum_{\Lambda^{(m-1)} \Lambda_1^{(m-1)}} (\lambda_1 \Lambda_2 | V_{12}(R, R_2) | \Lambda_1 \Lambda'_2)
\]  

\[
\times (2\pi i)^{-1} \int dw e^{-\beta W}(\Lambda^{(m-1)} | \Sigma_p[\ldots] | \Lambda^{(m-1)})
\]  

\[
= \left(\frac{z}{\gamma}\right)^{m-1} \int d^3 R^{(m-1)} (\lambda_1 | \text{Tr}^{(m-1)} (2\pi i)^{-1} \int dw e^{-\beta W}
\]  

\[
x \Sigma'_p V_{12}(R, R_2)(W - K^{m-1})^{-1} V_\mu \ldots V_\sigma(W - K^{m-1})^{-1} |\lambda'_1\rangle.
\]  

(5.13)
Fig. 5.
Note that in this last expression \( V_{12} \) has been placed under the summation sign, and accordingly noncyclic permutations of the \( V \)'s acting on the last \((m-1)\) molecules are to be taken. Figure 5 illustrates a term of Eq. (5.13), corresponding to Fig. 3.

We notice that Eq. (5.13) is analogous in form to (5.6). Hence we perform the set of operations analogous to those that led to Eq. (5.8) and ultimately to (5.11). We find then

\[
Q_m(R; \lambda_1, \lambda'_1) = (z/\tau) \int d^3 R_2 \sum_{\lambda_2 \lambda'_2} \langle \lambda_1 \lambda'_2 | V_{12} (R, R_2) | \lambda'_1 \lambda_2 \rangle \times (e'_2 - e_2)^{-1} [\exp(-\beta e'_2) - \exp(-\beta e_2)] Q_{m-1}(R_2; \lambda'_2, \lambda'_2) \cdot
\]

(5.14)

Let us now sum Eq. (5.11) over all \( m \) to obtain the simple-chain approximation to the polarization:

\[
F^{sc}(R) = \sum_{m=1}^{\infty} F^{sc}_m(R) = (z/\tau) \sum_{\lambda_1 \lambda'_1} Q(R; \lambda_1, \lambda'_1) \cdot
\]

(5.15)

where, from Eq. (5.14),

\[
Q(R; \lambda_1, \lambda'_1) \equiv \sum_{m=1}^{\infty} Q_m(R; \lambda_1, \lambda'_1) \cdot
\]

(5.16)

\[
= Q_1(R; \lambda_1, \lambda'_1) + (z/\tau) \int d^3 R' \sum_{\lambda_2 \lambda'_2} \langle \lambda_1 \lambda'_2 | V_{12} (R, R') | \lambda'_1 \lambda_2 \rangle \times (e'_2 - e_2)^{-1} [\exp(-\beta e'_2) - \exp(-\beta e_2)] Q(R'; \lambda_2, \lambda'_2) \cdot
\]

(5.17)
From Eqs. (5.11), (4.11), and (4.13), we see that $Q_1$ is

$$Q_1(R; \lambda_1, \lambda'_1) = - \langle \lambda_1 | p_1 | \lambda'_1 \rangle \cdot E_0(R) \cdot (5.18)$$

To solve the integral equation (5.17) for $Q$, let us divide the domain of integration into two parts,

I  \quad | R - R' | > R_0 ,

II  \quad | R - R' | < R_0 ,

where $R_0$ is large compared with molecular dimensions, but sufficiently small macroscopically so that $E_0$ may be considered constant over the distance $R_0$. In domain I we may approximate $\nu_{12}$ by Eq. (2.5):

$$\nu_{12}(R, R') = p_1 \cdot A(R, R') \cdot p_2 \cdot (5.19)$$

while in domain II we may set

$$Q(R'; \lambda_2, \lambda'_2) = Q(R; \lambda_2, \lambda'_2) \cdot (5.20)$$

since $Q$ varies as slowly as $E_0$. Equation (5.17) now reads

$$Q(R; \lambda_1, \lambda'_1) = - \langle \lambda_1 | p_1 | \lambda'_1 \rangle \cdot E_0(R)$$

$$\quad - (z/r) \int_I d^3R' A(R, R') \cdot \sum_{\lambda_2 \lambda'_2} Q(R'; \lambda_2, \lambda'_2) \cdot p_2(\lambda'_2, \lambda_2)$$

$$\quad + (z/r) \sum_{\lambda_2 \lambda'_2} Q(R; \lambda_2, \lambda'_2)(e'_2 - e_2)^{-1} [\exp(-\beta e'_2) - \exp(-\beta e_2)]$$

$$\quad \times \langle \lambda_1 \lambda'_2 | \int_{\text{II}} d^3R' \nu_{12} (R, R') | \lambda'_1 \lambda_2 \rangle . \quad (5.21)$$
The second term in the first square bracket of (5.21) is, by Eq. (5.15),

\[ - \int_1 d^3 R' \ A(R, R') \cdot \mathbf{P}^{sc}(R') \]  \tag{5.22}

We proceed to the evaluation of the integral over domain II; by Eq. (2.3), it is

\[ \int_1 d^3 R' \ V_{12}(R, R') = \int_1 d^3 R' \int d^3 r \int d^3 r' \ \epsilon_1(x) \epsilon_2(x') (|R - R' + x - x'|^{-1}) \]

\[ = \int d^3 r \int d^3 r' \ \epsilon_1(x) \epsilon_2(x') \frac{4}{3} \pi |x \cdot x'| \]

\[ = \frac{4}{3} \pi \mathbf{P}_1 \cdot \mathbf{P}_2 \]  \tag{5.23}

Equation (5.21) thus becomes, with the help of (5.15),

\[ Q(R; \lambda, \lambda_1) = - \langle \lambda_1 | \mathbf{P}_1 | \lambda_1 \rangle \cdot \left[ \mathbf{E}_0(R) \right. \]

\[ - \int_1 d^3 R' \ A(R, R') \cdot \mathbf{P}^{sc}(R') - \frac{4}{3} \pi \mathbf{P}^{sc}(R) \]  \tag{5.24}

or with Eq. (3.5),

\[ Q(R; \lambda, \lambda_1) = - \langle \lambda_1 | \mathbf{P}_1 | \lambda_1 \rangle \cdot \mathbf{P}^{sc}(R) \]

\[ \]  \tag{5.25}

We substitute into (5.16) and obtain, with the help of Eq. (4.14),

\[ \mathbf{P}^{sc}(R) = z \alpha_1 \cdot \mathbf{P}^{sc}(R) \]  \tag{5.26}

In the simple-chain approximation, the susceptibility, defined by Eq. (3.19), is thus

\[ \chi^{sc} = z \alpha_1 \]  \tag{5.27}
and the dielectric constant

\[ K = 1 + 4\pi \chi \]  \hspace{1cm} (5.28)

is

\[ K^{sc} = 1 + 4\pi z \alpha_1. \] \hspace{1cm} (5.29)

It would be better to refer to the simple-chain summation not as an approximation, but as an introduction to the calculation of the next section. We shall see there that the assumption of only one interaction between two distant molecules is a good approximation; but it is clear that for two molecules which are close together this is a poor approximation. A simple model due to Kirkwood\(^{16}\) allows a considerable improvement. We reduce \( R_0 \) to molecular size, continue to use Eq. (5.19) in domain I, and drop the integration over domain II by invoking the hard-sphere model for the molecules, to prevent overlap. The last term of Eq. (5.24) is thus dropped, and (5.26) becomes

\[ P^{sc}(R) = z \alpha_1 \cdot \left[ E^{sc}(R) + \frac{4\pi}{3} P^{sc}(R) \right]. \] \hspace{1cm} (5.30)

If we now set \( z = n \) (low density), we obtain the Clausius-Mossotti formula,

\[ \frac{K - 1}{K + 2} = \frac{4\pi}{3} n \alpha_1. \] \hspace{1cm} (5.31)
VI. THE CLUSTER-CHAIN EXPANSION

In this section we define the type of graph called a "cluster chain," and calculate the contribution of all cluster chains to the polarization. We then show that under certain conditions all other graphs make a negligible contribution, so that the cluster-chain approximation is a satisfactory one.

For any graph of \( m \) molecules, we hold the positions of the molecular centers of mass fixed. If the distance between two interacting molecules is less than \( R_0 \) (where \( R_0 \) is small macroscopically, but large microscopically), the molecules are said to belong to the same cluster. Any interaction between two molecules in different clusters must therefore be over a distance greater than \( R_0 \). Note that two noninteracting molecules in different clusters may be nearer than \( R_0 \), and that two molecules in the same cluster may be farther apart than \( R_0 \). A cluster chain is now defined as a graph for which the topology of the interactions between clusters is analogous to that of a simple chain. We may number the clusters \( 8 = I, II, \ldots, M \), so that \( 8 \) and \( 8 + 1 \) have one and only one interaction, and \( I \) and \( M \) each interact once with the external field. See Fig. 6 for a three-cluster chain analogous to the simple chain of Fig. 3.

Consider an \( m \)-molecule \( M \)-cluster chain, with \( m_8 \) molecules in cluster \( 8 \). Let us assign the molecules to the numbered clusters, and multiply by \( m!/ \prod_{8} m_8! \), the number of such assignments. Then holding \( M \) fixed, we sum over all values of \( m_8 \) from one to infinity (thus summing over \( m \)). In this process we count each graph twice (as with simple chains), therefore we must correct with a factor \( \frac{1}{2} \). Equations (3.26) and (3.27) can thus be replaced by
Fig. 6.
In expression (6.3), we have \( m = \Sigma m_\delta \), and \( L \) selects cluster chains characterized by the set \( \{m_\delta\} \).

The \( m \)-molecule Hamiltonian \( H^m \) for an \( M \)-cluster chain may be written as

\[
H^m = K^{(M)} + V^{(M)},
\]

where

\[
K^{(M)} = \Sigma H_\delta
\]

is the sum of the cluster Hamiltonians \( H_\delta \), and

\[
V^{(M)} = V_I + \sum_{\delta=1}^{M-1} V_{\delta,\delta+1} + V_M
\]

includes the intercluster interactions \( V_{\delta,\delta+1} \) and the external interactions \( V_I \) and \( V_M \). Thus the external interaction \( V_I \) is

\[
V_I = -\Sigma R_i \cdot E_0(R_i)
\]

and the intercluster interaction \( V_{II} \) is

\[
V_{II} = \Sigma \Sigma P_j \cdot \Delta(R_j, R_k) \cdot P_k
\]

since \( R_{jk} > R_0 \) if molecules \( j \) and \( k \) interact. The cluster Hamiltonian \( H_\delta \) includes the internal Hamiltonians of the \( m_\delta \) molecules and the intracluster
interactions of these molecules. The trace in Eq. (6.3) is to be taken over properly antisymmetrized cluster states, but electron exchange between clusters may be neglected because of their separation.\textsuperscript{17} The integration over molecular positions in (6.3) is subject to the restrictions of the definition.

The development of Eq. (6.3) is now completely analogous to that of Eq. (5.1). We may thus immediately write down the analogue of Eq. (5.8):

\[
\mathcal{I}_M = -\frac{1}{2} \beta \sum_{\{m_8\}} \frac{z^m}{\gamma} \prod_{i=0}^m m_8! \int d^3R(m) L^{(m_8)} \text{Tr} \left\{ V_{\text{I II}} \right. \\
\times \left. \left[ (2\pi i)^{-1} \int d\omega e^{-\beta\omega} \sum_{P} (W - K^{(M-1)})^{-1} V_{\mu} \cdots V_{\nu} (W - K^{(M-1)})^{-1} \right] \right. \\
\times \left. (2\pi i)^{-1} \int d\omega e^{-\beta\omega} (W - H_\text{I})^{-1} V_{\text{I}} (W - H_\text{I})^{-1} \right\}. \tag{6.9}
\]

To find the polarization (Eq. 6.2), we differentiate only with respect to the \(E_0\) in \(V_{\text{I}}\) (see Eq. 6.7) and multiply by 2:

\[
\mathcal{E}_M(R) = \sum_{\{m_8\}} \frac{z^m}{\gamma} \prod_{i=0}^m m_8! \int d^3R(m) L^{(m_8)} \text{Tr} \\
\times \left\{ (2\pi i)^{-1} \int d\omega e^{-\beta\omega} (W - H_\text{I})^{-1} \sum_{\text{I}} \sum_{\text{II}} \varepsilon_{\text{I}} \varepsilon_{\text{II}} \sum_{j,k} \varepsilon_{\text{j}} \cdot \mathbf{A}(\mathbf{R}_j, \mathbf{R}_k) \cdot \mathbf{B}_k \right\}. \tag{6.10}
\]

We have used Eq. (6.8) for \(V_{\text{I II}}\), and the symbol \([\ldots]\) for the square-bracketed quantity in Eq. (6.9).

Let us extract from Eq. (6.10) the quantities referring to cluster I, performing the integration over all molecular positions except those of
molecules $i$ and $j$. For $i = j$ we have (setting $\frac{m}{m} = m$ here)

$$\rho^{(1)} = \sum_{m=1}^{\infty} \frac{z^m}{m!} \int d\mathbf{R}^{(m-1)} L \text{Tr}(2\pi i)^{-1} \int dw e^{-\beta w(w-H)^{-1}} p_1(w-H)^{-1} p_1,$$

(6.11)

since the $m$ terms in the sum over $i$ are equivalent. For $i \neq j$ we have

$$\rho^{(2)}(\mathbf{R}_1, \mathbf{R}_2) = \sum_{m=1}^{\infty} \frac{z^m}{m!} \int d\mathbf{R}^{(m-2)} L \text{Tr}(2\pi i)^{-1}$$

$$\times \int dw e^{-\beta w(w-H)^{-1}} p_1(w-H)^{-1} p_2 .$$

(6.12)

The spatial integration is subject to the restrictions on molecular positions implied in the definition of a cluster.

The polarization (Eq. 6.10) is thus

$$\mathcal{P}^M(\mathbf{R}) = \int d\mathbf{R} \mathcal{Q}(\mathbf{R}, \mathbf{R}') \cdot \sum_{\{m_{\delta}\}} \frac{z^m}{m!} \int d\mathbf{R}^{(m)} L^{(m_{\delta})}$$

$$\times \sum_k \Lambda(\mathbf{R}', \mathbf{R}_k) \cdot \text{Tr} \{ p_k \{ \ldots \} \} ,$$

(6.13)

where

$$\mathcal{Q}(\mathbf{R}, \mathbf{R}') = \rho^{(1)}(\mathbf{R} - \mathbf{R}', \mathbf{R}) + \rho^{(2)}(\mathbf{R}, \mathbf{R}') .$$

(6.14)

In Eq. (6.13), the quantities $m, m_{\delta}, L^{(m_{\delta})}$ refer to the $(M-1)$-cluster chain exclusive of the first cluster.

An expression for $\mathcal{P}^{M-1}$ is obtainable from the analogue of Eq. (5.6)

if $V_{II}$ is chosen to stand outside the sum. We then have
\[ L^{M-1}(\mathbf{R}) = \sum_{\{m_0\}} \frac{z^m}{\gamma^m} \int d^3 \mathbf{m} P_0^{(m)} \left( \mathbf{R}_0 \right) \left\{ \text{Tr} \left[ \sum_k \mathbf{R}_k \delta(\mathbf{R} - \mathbf{R}_k) \right] \right\}. \]  

(6.15)

Upon comparing this with Eq. (6.13), we find

\[ L^M(\mathbf{R}) = \int d^3 \mathbf{R}' \mathbf{G}(\mathbf{R}, \mathbf{R}') \cdot \int d^3 \mathbf{R}'' \mathbf{A}(\mathbf{R}', \mathbf{R}'') \cdot L^{M-1}(\mathbf{R}''). \]  

(6.16)

For \( M = 1 \), on the other hand, we easily obtain

\[ L^1(\mathbf{R}) = -\int d^3 \mathbf{R}' \mathbf{G}(\mathbf{R}, \mathbf{R}') \cdot \mathbf{E}_0(\mathbf{R}'). \]  

(6.17)

We thus find, for the sum of all cluster chains (Eq. 6.1),

\[ L(\mathbf{R}) = -\int d^3 \mathbf{R}' \mathbf{G}(\mathbf{R}, \mathbf{R}') \left[ \mathbf{E}_0(\mathbf{R}') - \int d^3 \mathbf{R}'' \mathbf{A}(\mathbf{R}', \mathbf{R}'') \cdot L(\mathbf{R}'') \right]. \]  

(6.18)

From the cluster-chain definition, the integration over \( \mathbf{R}'' \) excludes a sphere of radius \( R_0 \) about \( \mathbf{R}' \) (see Eq. 6.10 for the original appearance of \( \mathbf{A} \)).

Hence, by Eq. (3.5), this relation is

\[ L(\mathbf{R}) = -\int d^3 \mathbf{R}' \mathbf{G}(\mathbf{R}, \mathbf{R}') \left[ \mathbf{E}(\mathbf{R}') + \frac{4}{3} \pi \mathbf{E}(\mathbf{R}') \right]. \]  

(6.19)

Equations (3.5) and (6.19) provide coupled integral equations from which the polarization \( L(\mathbf{R}) \) and the electric field \( \mathbf{E}(\mathbf{R}) \) may be determined from the external field \( \mathbf{E}_0(\mathbf{R}) \). When the field vary slowly over microscopic dimensions, these equations may be simplified. Let us assume that the density is sufficiently low (and hence the activity also) that the sum over \( m \) in Eqs. (6.11) and (6.12) can be truncated at a finite \( m \). From the cluster definition, \( \mathbf{G}(\mathbf{R}, \mathbf{R}') \) is then defined only for \( |\mathbf{R} - \mathbf{R}'| \) less than some finite multiple of \( R_0 \), thus restricting the \( \mathbf{R}' \) integration in Eq. (6.19).

We choose \( R_0 \) so small that \( L(\mathbf{R}) \) (and therefore \( \mathbf{E} \)) are effectively constant over the \( \mathbf{R}' \) integration, and obtain
where 1

Since A is a constant tensor, it must be scalar:

A = A \mathbb{I} ,

where

A = - \frac{1}{3} \text{Sp} \int d^3 \mathbf{r}' \mathbf{g}(\mathbf{r}, \mathbf{r}') ,

so that

\mathfrak{F}(\mathbf{r}) = A \left[ \mathbf{E}(\mathbf{r}) + \frac{4 \pi}{3} \mathbf{P}(\mathbf{r}) \right] .

This is of the form of (Eq. 3.19), with

\chi = \frac{A}{1 - \frac{4}{3} \pi A} .

If we introduce the dielectric constant K,

K = 1 + 4 \pi \chi ,

we find that $\frac{4}{3} \pi A$ equals the Clausius-Mossotti expression:

\frac{K - 1}{K + 2} = \frac{4}{3} \pi A .

Referring to Eqs. (6.21), (6.14), (6.11), and (6.12), we see that

A = \sum_{m=1}^{\infty} z^m A'_m ,

where
is the (temperature-dependent) polarizability of an m-molecule linked cluster; 
\( p_{(m)} \) is the total dipole moment of the cluster. To obtain an expansion in
powers of the mean molecular density \( n = N/V \), we use Eq. (3.42) of paper I,

\[
  n = \sum_{m=1}^{\infty} m^m b_m ,
\]

(6.30)

where \( b_m \) is the cluster integral defined by Eq. (3.39) of I, and \( b_1 = 1 \).
As stated above, for consistency \( X \) should be evaluated in the zero-field
limit; hence in Eq. (6.30) both \( z \) and \( b_m \) refer to the zero-field case, or
\( r = 0 \) in the notation of Sec. V of I. Let us solve Eq. (6.30) for \( z(n) \):

\[
  z = n - 2 b_2 n^2 + \cdots ,
\]

(6.31)

and substitute into Eq. (6.28). We then find

\[
  \alpha = \sum_{m=1}^{\infty} n^m \alpha_m ,
\]

(6.32)

with \( \alpha_1 \equiv \alpha'_1 \), the single-molecule polarizability of Sec. IV,

\[
  \alpha_2 \equiv \alpha'_2 - 2b_2 \alpha_1 ,
\]

(6.33)

and so forth. Since the \( \alpha'_m \) and \( \alpha_m \) are all scalar tensors, we may write
Eq. (6.27) as

\[
  \frac{K - 1}{K + 2} = \frac{4}{3} \pi \sum_{m=1}^{\infty} n^m \alpha_m
\]

(6.34)

\[
  = \frac{4}{3} \pi (n \alpha_1 + n^2 \alpha_2 + \cdots) .
\]

(6.35)
The Clausius-Mossotti function is thus expressed as a power series in density; the first term of the series yields the conventional Clausius-Mossotti formula, while the $\alpha_2$ term gives the first correction to it. In a subsequent paper we shall discuss the evaluation of $\alpha_2$ from Eqs. (6.33) and (6.29), and shall relate it to the work of previous investigators.\footnote{11}

We must now inquire into the validity of the cluster-chain approximation. It is clear from the result (Eq. 6.34) that it is a low-density approximation, and can be valid only if the series (6.34) converges. We therefore do not expect it to be valid for a condensed state.

Let us now consider the contribution of a graph, such as shown in Fig. 7, which is not a cluster chain. Let us first select the set of clusters I, II, III, whose successive linkages (with the external field and with one another) are those of a chain, except that successive clusters may be multiply linked. Each additional linkage (V$_{\text{I II}}$ in this case) introduces an additional factor of the order of

$$< V_{\text{I II}} > / \Delta E,$$  \hspace{1cm} (6.36)

where $< V_{\text{I II}} >$ is a matrix element of the order of

$$< p_{\text{I}} > < p_{\text{II}} > / (R_{\text{I II}})^3,$$  \hspace{1cm} (6.37)

with $< p_{\text{I}} >$, $< p_{\text{II}} >$ representing dipole moment matrix elements, $R_{\text{I II}}$ the separation of the molecules undergoing the additional interaction, and $\Delta E$ a typical energy difference. Since the polarizability $\alpha_1$ is of the order of $< p >^2 / \Delta E$, and since $R_{\text{I II}}$ must be greater than $R_0$, the additional factor (6.36) is of the order of

$$\alpha_1 / R_0^3.$$  \hspace{1cm} (6.38)
Thus, in order to neglect a graph having multiple linkage, it is necessary to choose $R_0$ sufficiently large that $(6.38)$ is very small. Since $\alpha_1$ is typically of the order of a molecular volume, this should in general be possible if the field $E_0$ does not vary significantly over molecular dimensions.

The other clusters IV, V, VI are connected to the chain I-II-III either by one linkage (IV) or by two or more (V, VI). In the latter case, the number of linkages exceeds the number of additional clusters, thus introducing a number of factors $(6.36)$ equal to the excess. The argument above then makes the relative contribution negligible. In the former case, the single linkage couples the cluster(s) concerned through its mean dipole moment in the absence of a field; by the isotropy of the cluster Hamiltonian, such a graph then vanishes.

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APPENDIX

We wish to prove the Hugenholtz theorem in a form suitable for use in Section V. Consider two uncoupled systems, 1 and 2, with the respective Hamiltonians

\[ H_\alpha = K_\alpha + V_\alpha \]

for \( \alpha = 1, 2 \).

The total Hamiltonian is

\[ H = K + V , \]

with \( K = \sum_\alpha K_\alpha \), and \( V = \sum_\alpha V_\alpha \).

Because the two systems do not interact, their Hamiltonians commute, and we have

\[ e^{-\beta H} = \sum_\alpha e^{-\beta H_\alpha} , \]

or

\[ (2\pi i)^{-1} \int dW e^{-\beta W (W - H)^{-1}} = \prod_\alpha (2\pi i)^{-1} \int dW_\alpha e^{-\beta W_\alpha (W_\alpha - H_\alpha)^{-1}} . \]

We expand \((W_\alpha - H_\alpha)^{-1}\) as in paper I, and consider a particular graph for each \( \alpha \), corresponding to a single term in the expansion. Such a graph is characterized by the order in which the component terms (interactions) of \( V_\alpha \) appear. For each graph of 1 and 2, there are a number of (unlinked) graphs of the composite system, in which the order of interactions is maintained within each part \( \alpha \), but with different order of the \( V_\alpha \) interactions relative to the \( V_\beta \) interactions. The corresponding terms in the expansion of Eq. (A.1) express this relation algebraically.
REFERENCES AND FOOTNOTES

6. For derivations of this expansion, see (e.g.) Mayer and Mayer, Statistical Mechanics (John Wiley and Sons, New York, 1940); T. L. Hill, Statistical Mechanics (McGraw-Hill Book Company, New York, 1956); and the review paper by J. DeBoer, Repts. Progr. in Phys. 12, 305 (1949).
8. A reading of paper I is helpful but not essential to an understanding of this paper.
9. We plan to discuss the nonlinear effects in a future paper.
10. A formal expansion of the same type as Eq. (6.34) has previously been derived by T. Hill, J. Chem. Phys. 28, 61 (1958), using the Ono-Kilpatrick approach.
12. Precise definitions of \( \varepsilon \) and of the polarization are given in Section III.
13. W. F. Brown, op. cit. (Ref. 11), Sec. 2.
17. A precise formulation of the application of the Pauli principle to all
   the electrons of the graph may be based on the considerations of paper I.
   It is shown there that proper consistent use of the linkage operator \( L \)
   allows one to limit antisymmetrization to the electrons of a cluster
   (as defined in I). Similar considerations may be applied here.
18. For a polar gas, \( \alpha_1 \) may be a thousand times the molecular volume, but
   even so a suitable \( R_0 \) can usually be chosen.
FIGURE CAPTIONS

1. The single-molecule graph.
2. A simple chain for \( m = 3 \).
3. A simple chain differing from that of Fig. 2 by a cyclic permutation of the interactions.
4. The simple chain of Fig. 2, unlinked by the removal of \( V_{12} \).
5. The simple chain of Fig. 2, less molecule 1.
6. A cluster chain analogous to the simple chain of Fig. 3.
7. A graph which is not a cluster chain.
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